

RUSTEM VALIULLIN

# EXPERIMENTAL PHYSICS SCRIPTS

FELIX BLOCH INSTITUTE FOR SOLID STATE PHYSICS, AP-  
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# 1 Thermodynamics

THIS CHAPTER covers various topics from kinetic gas theory to phase transitions.

## 1.1 Kinetic gas theory

AROUND 1900 the Maxwell's electromagnetic theory was so successful, that many scientists believed that all physical behavior is ultimately electromagnetic, henceforth continuous. As an interesting historical example, irrespective of an enormous contribution of Boltzmann to statistical physics based on the concept of atoms to that date, he was not even invited to the physics section at a physics conference in St. Louis in 1904. It seemed like most physicists rejected atoms and atomistic structure. In this section, we will cover an important phenomenon, which critically contributed to the justification of atomistic theory. The kinetic gas theory is also a very instructive topic to move from Newtonian mechanics covered in the last semester to thermodynamics. It provides with an intuitive understanding of such complex phenomena like temperature, pressure or energy.

### 1.1.1 Gas pressure

Let us start with an idealization that air in a reservoir may conceptually be modeled with a collection of small balls (atoms or molecules, from now on will be used as synonyms) each having mass  $m$  and velocity  $\vec{v}_i$ , where the index  $i$  refers to a specific velocity. Essentially, and reasonably, we let the velocities to be somehow distributed. Let us also assume that these balls move chaotically. Indeed, reasonably non-central inter-ball collisions will be responsible for randomisation of the flight directions. From time to time the atoms may also collide with the reservoir walls. We will consider the collision events to be elastic, i.e. to occur without energy change. Let us select a small area

Later we will see that this distribution is not arbitrary and there are common physical rules governing them.

element  $dA$  on the wall of a reservoir of a volume  $V$  and containing  $N$  atoms and calculate pressure exerted to it due to the atoms colliding this area. For performing the derivations, let us consider a sub-ensemble of the atoms having the velocity  $v_{ix}$  normal to the wall as shown in Figure 1.1. With the help of this figure, it can be seen that the collisions frequency with  $dA$  can be found by considering only the atoms initially found in the volume element  $v_{ix}dA\Delta t$ . Indeed, an atom positioned at a distance  $l > v_{ix}\Delta t$  (atom 1 in the figure), cannot approach the wall during  $\Delta t$ . On the other hand, an atom outside the volume considered (e.g. atom 2 in the figure) has a chance to hit  $dA$ . However, we drop it out of the consideration, because there is an equivalent atom within the volume which may not hit  $dA$  due to an inappropriate combination of  $v_y$  and  $v_z$ .

As the next step, let us consider a collision event of an individual atom with the wall. Let us separate the whole process on two steps as shown in Figure 1.2: (1) collision with the wall followed by the ball contraction and (2) restoring the ball shape followed by flight out of the wall. In finding the linear momentum change during these two processes, we will omit its  $y$ - and  $z$ -components because they remain unchanged. Thus, the momentum change in the first stage is

$$\Delta p_{ix,1} = -mv_{ix} = -p_{ix} \quad (1.1)$$

The total momentum change during  $dt$  is found as

$$\Delta p_{x,1} = \sum_{v_{ix}>0} -p_{ix} \frac{N_i}{V} v_{ix} dA \Delta t \quad (1.2)$$

Here,  $N_i/V$  represents the number density of atoms having  $v_{ix}$ . From the mechanics we know that the force  $dF_{x,1}$  needed for the momentum change  $\Delta p_{x,1}$  is

$$dF_{x,1} = \frac{\Delta p_{x,1}}{\Delta t} = \sum_{v_{ix}>0} p_{ix} \frac{N_i}{V} v_{ix} dA \quad (1.3)$$

In the similar way the second stage is treated. Here, the "compressed" atom restores its shape and thus exerts force on the surface:

$$dF_{x,2} = \frac{\Delta p_{x,2}}{\Delta t} = \sum_{v_{ix}<0} p_{ix} \frac{N_i}{V} v_{ix} dA \quad (1.4)$$

Note that in Eq. 1.4 the summation is performed over the atoms having negative velocities, i.e. moving outwards the wall. Finally, pressure is found as

$$P = \frac{dF_{x,1} + dF_{x,2}}{dA} = \frac{1}{V} \sum_i N_i v_{ix} p_{ix} \quad (1.5)$$

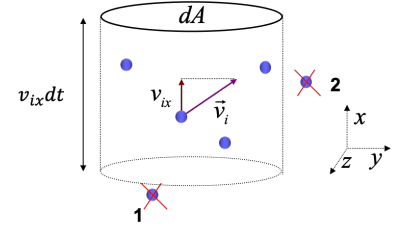


Figure 1.1: Atoms colliding with the reservoir wall

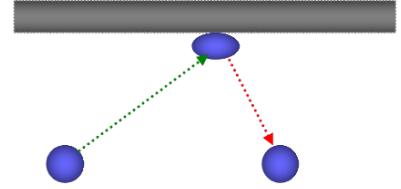


Figure 1.2: Two stages of collision

It turns out that pressure is determined by the ensemble averaged value of the product of the normal (to surface) components of linear momentum and velocity:

$$P = \frac{N}{V} \langle v_x p_x \rangle \quad (1.6)$$

For isotropic systems,

$$\langle \vec{v} \vec{p} \rangle = \langle v_x p_x \rangle + \langle v_y p_y \rangle + \langle v_z p_z \rangle \quad (1.7)$$

Hence, quite generally,

$$PV = \frac{1}{3} \langle \vec{v} \vec{p} \rangle = \frac{2}{3} \langle E_{k,total} \rangle \quad (1.8)$$

It turns thus out that the product of pressure and volume is found to be two-thirds of the average kinetic energy of the gas contained in the reservoir. Qualitatively, this result is not surprising - indeed we have discussed in the mechanics course that pressure is nothing else than the energy density. Here we have established, however, also the quantitative pre-factor.

$$\langle x \rangle \equiv \frac{\sum_i N_i x_i}{\sum_i N_i}$$

### 1.1.2 Kinetic interpretation of temperature

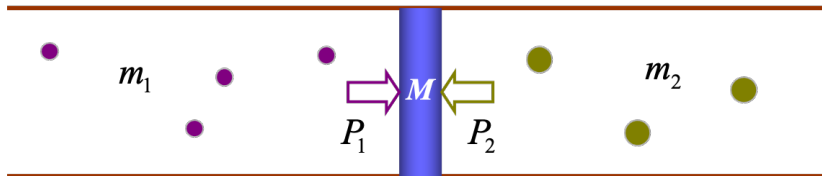


Figure 1.3: Frictionless piston in a tube

The idealised gas model allows establishing some general properties of the average kinetic energy. Let us consider a tube containing a frictionless piston of mass  $M$  as shown in Figure 1.3. On two sides of the piston the tube is filled with different gases having different masses and containing different amounts of atoms. In equilibrium the pressures exerted on the piston by two gases must obviously be identical:  $P_1 = P_2$ . Hence, according to Eq. 1.8, must also be equal the following quantities:

$$m_1 n_1 \langle v_1^2 \rangle = m_2 n_2 \langle v_2^2 \rangle, \quad (1.9)$$

where  $n_1$  and  $n_2$  are the respective number densities or concentrations. However, as we will see in what follows, this is not sufficient for equilibrium, the temperatures must be identical as well. Let us find in a mechanistic way the meaning of temperature. For this, we consider the conservation of linear momentum. Let us consider an

atom colliding with the piston. With the prime quantities we will denote the ones after the collision. The conservation law says

$$m_1 v_{1x} + Mu = m_1 v'_{1x} + Mu', \quad (1.10)$$

where  $u$  and  $u'$  are the piston velocities. For the elastic collision also the total kinetic energy should not change:

$$m_1 v_{1x}^2 + Mu^2 = m_1 v_{1x}'^2 + Mu'^2, \quad (1.11)$$

The system of two equations can be solved to find  $v_{1x}'^2$ :

$$v_{1x}'^2 = \frac{4M^2 u^2 + 4M(m_1 - M)^2 u v_{1x} + (m_1 - M)^2 v_{1x}^2}{(m_1 + M)^2} \quad (1.12)$$

By taking the ensemble average on both sides one finds

$$\langle v_{1x}'^2 \rangle = \frac{4M^2 \langle u^2 \rangle + (m_1 - M)^2 \langle v_{1x}^2 \rangle}{(m_1 + M)^2} \quad (1.13)$$

If the system is in equilibrium, then  $\langle v_{1x}'^2 \rangle = \langle v_{1x}^2 \rangle$ . Hence, Eq. 1.13 simplifies to

$$\frac{1}{2} m_1 \langle v_{1x}^2 \rangle = \frac{1}{2} M \langle u^2 \rangle \quad (1.14)$$

Equivalently, the right part of the tube may be treated to yield

$$\frac{1}{2} m_2 \langle v_{2x}^2 \rangle = \frac{1}{2} M \langle u^2 \rangle \quad (1.15)$$

By comparing Eqs. 1.14 and 1.15 it is thus seen that in equilibrium the  $x$ -component of the average kinetic energies of the two gases must be identical. In the absence of any interaction fields the average square velocity components are identical, hence the aforementioned statement is applicable to the average kinetic energy in general.

What we see is that if the average kinetic energies of the atoms on two sides of the piston are different, then the collisions with the piston will eventually lead to their equilibration. But this is the property of temperature known from our everyday experience! Indeed, two bodies with different temperatures brought into contact will later have the same temperature. Hence, we may introduce a "kinetic" temperature

$$\Theta \equiv \frac{2}{3} \langle E_k \rangle \quad (1.16)$$

or a more conventional thermodynamic temperature  $T$  as

$$\Theta \equiv kT, \quad (1.17)$$

Note that the kinetic energy conservation is written here in the component form, which is generally wrong. In this particular case it is justified while the piston can move only along  $x$ , hence the  $y$ - and  $z$ -components of linear momentum are conserved, hence the energy components too.



where  $k$  is a constant known as the Boltzmann constant. With this definition, Eq. 1.8 assumes a well-known form

$$PV = NkT \quad (1.18)$$

which was empirically established long before the foundation of thermodynamics or kinetic gas theory. The derivation performed along the gas kinetic theory provides a very clear physical meaning of this equation, except the fact that the existence of atoms that days was not yet accepted.

### 1.1.3 The equipartition theorem

Interestingly, the derivation of the last section yields another very important property of any thermodynamic system, which is known under the name "equipartition theorem". By combining Eqs. 1.17 and 1.17, the average kinetic energy results as

$$\langle E_k \rangle = 3 \left( \frac{1}{2} kT \right) \quad (1.19)$$

The theorem says that in thermodynamic equilibrium there is an average kinetic energy of  $kT/2$  per object and per degree of freedom. The gas particles, idealised balls, have three translational degrees of freedom associated with each cartesian coordinate.

What about the piston, whose center of mass has only one degree of translational freedom? The theorem says in this regard that

$$\frac{1}{2} M \langle u^2 \rangle = \frac{1}{2} kT \quad (1.20)$$

What about the individual atoms composing the piston? Let us express the center-of-mass velocity  $u$  of the piston as a function of velocities  $u_k$  of the individual atoms:

$$u = \frac{1}{M} \sum_k m_k u_k \quad (1.21)$$

By squaring it and taking the average, the mean kinetic energy of the piston is It is more intuitive to consider the time average and keep in mind that, for ergodic systems, time and ensemble averages are equivalent.)

$$\frac{1}{2} M \langle u^2 \rangle = \frac{1}{2M} \left\langle \sum_k m_k u_k \sum_j m_j u_j \right\rangle \quad (1.22)$$

Because in equilibrium the velocities of different atoms are uncorrelated, the only the terms with  $k = j$  survive averaging in Eq. 1.22:

$$\frac{1}{2}M\langle u^2 \rangle = \frac{1}{2M} \sum_k m_k^2 \langle u_k^2 \rangle \quad (1.23)$$

If we assume that all atoms have the same mass and by noting Eq. 1.20 we find

$$\frac{1}{2}m_k \langle u_k^2 \rangle = \frac{1}{2}kT \quad (1.24)$$

Remarkably, each atom constituting the piston as well has an average energy of  $kT/2$ , the same as for the piston! The same applies also for the objects, like big polymer chains - their average total energy is  $3kT/2$ , the average energies of the atoms composing the chains is  $3kT/2$ .

The partition theorem applies also to other degrees of freedom rather than only translational ones and not only for kinetic but also the potential energy. Each time when energy is quadratic in terms of velocity or position, it contributes with  $kT/2$  to the total average energy. A good example of this phenomenon is given by the temperature dependencies of the heat capacity (energy) of polyatomic molecules. As an example, Figure 1.5 shows schematically energy of a diatomic molecule, such as of  $H_2$  in Figure 1.4. At very low temperatures, the total average energy is  $3kT/2$  and results from translational motion. The vibrations and rotations of the molecules at these temperatures are suppressed. At higher temperatures (e.g. about room temperatures and higher for hydrogen molecule) molecular rotations contribute by  $kT$ . At notably higher temperatures (several thousands Kelvin for  $H_2$ ) the vibrations become appreciable and also contribute by  $kT$ . In the latter case the half comes from the kinetic energy and half from the potential energy.

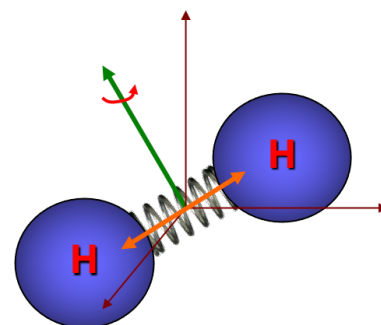


Figure 1.4: Hydrogen molecule  
Note that the equipartition law can be violated at low temperatures when the quantum effects set in.

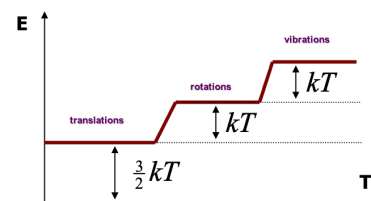


Figure 1.5: Energy of a diatomic molecule as a function of temperature

#### 1.1.4 Maxwell distribution of velocities

So far we have assumed that the atomic velocities and speeds are not identical and are somehow distributed. Is this distribution arbitrary or is it subject to some restrictions under equilibrium conditions? The answer is that this distribution has a well-defined form given known as the Maxwell distribution of velocities. We will not derive this law rigorously, rather obtain it in an empiric way.

Let us assume that the distribution of the velocity components is given by the unknown functions  $\varphi(v_i)$ , where  $i = x, y, z$ . If the functions are normalized, i.e. if  $\int_{-\infty}^{\infty} \varphi(v_i) dv_i = 1$  then  $\varphi(v_x) dv_x$  has a meaning of probability that for an arbitrarily selected atom the velocity component  $v_x$  is between  $\varphi(v_x)$  and  $\varphi(v_x) + dv_x$ . For isotropic systems the probabilities that the atoms move in positive and negative directions are identical, i.e.  $\varphi(v_i) = \varphi(-v_i)$ . This suggest that the

argument of the distributions functions should be  $v_i^2$  rather than  $v_i$ . More convenient is to use, however, the kinetic energy components  $E_{ki}$ .

For the distribution of the velocities (not its components!), we introduce another function  $F(\vec{v})$ . Because the velocity components are independent,

$$F(\vec{v}) = \varphi(v_x)\varphi(v_y)\varphi(v_z) \quad (1.25)$$

If now to take account of the equivalency of the directions, Eq. ?? can be rewritten

$$F(E_{kx} + E_{ky} + E_{kz}) = \varphi(E_{kx})\varphi(E_{ky})\varphi(E_{kz}) \quad (1.26)$$

The simplest function  $\varphi$ , which has the property of Eq. 1.26, is the exponential function. Thus, a good guess (which as well turns out to be the proper one) is

$$\varphi(E_{ki}) = Ae^{-\alpha E_{ki}} \quad (1.27)$$

where  $A_i$  and  $\alpha$  are the positive constants. They can be easily established using the following arguments. First of all, the functions  $\varphi(\varphi_i)$  are normalized, hence

$$A \int_{-\infty}^{\infty} \exp\left\{-\frac{1}{2}\alpha m v_i^2\right\} dv_i = 1 \quad (1.28)$$

By using the equipartition theorem, the average energy per translational degree of freedom is also known:

$$A \int_{-\infty}^{\infty} \frac{1}{2} m v_i^2 \exp\left\{-\frac{1}{2}\alpha m v_i^2\right\} dv_i = \frac{1}{2} kT \quad (1.29)$$

By solving these two equations the final form for the velocity components and the velocity are found respectively as

$$\varphi(v_i) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left\{-\frac{m v_i^2}{2kT}\right\} \quad (1.30)$$

and

$$F(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{m v^2}{2kT}\right\} \quad (1.31)$$

Figure 1.6 shows the distribution of the molecular velocity components in air at ambient conditions. These are expectedly symmetric functions about zero velocity with relatively long tails. Thus, for hydrogen molecules the velocities are seen to extend over several kilometers per second.

In Eqs. 1.25 and 1.26 the same notions  $\varphi$  and  $F$  are used, however they are different in these equations.

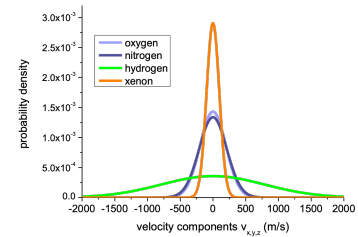


Figure 1.6: Distributions of molecular velocities in atmosphere

Distribution of molecular velocities in the atmosphere explains in particular why the Moon has no atmosphere while Earth has it?

## 1.1.5 The Maxwell distribution of speeds

It is more instructive to consider in some details the speed rather than velocity distributions. Because all propagation directions are equivalent, the fraction of atoms having velocity  $v$  will be proportional to  $4\pi v^2$ . Hence, the speed distribution function is simply the product of Eq. 1.31 with  $4\pi v^2$ :

$$F(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 \exp \left\{ -\frac{mv^2}{2kT} \right\} \quad (1.32)$$

They are shown in Figure 1.7 for oxygen and hydrogen as selected examples. These are now asymmetric, bell-shaped functions. In many case, simple characteristics of atomic or molecular motions are needed. Typically, there are three quantities which are often used in the literature: the average, most probable, and root-mean-square (r.m.s.) speeds. The most probable speed  $v_m$  corresponds with the fraction of atoms having the highest speed. It is, henceforth, easily found as an extremum of Eq.1.32:

$$\frac{dF(v)}{dv} = 0 \quad (1.33)$$

resulting in

$$v_m = \sqrt{\frac{2kT}{m}} \quad (1.34)$$

The average speed  $\langle v \rangle$  is found by averaging the quantity we are looking for over the respective distribution function:

$$\langle v \rangle = \int_0^\infty v F(v) dv \quad (1.35)$$

This yields

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \quad (1.36)$$

Finally, for finding the r.m.s. speed the equipartition theorem may be used which readily yields

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} \quad (1.37)$$

A classical **experiment** for verifying the Maxwell distribution of velocities has been performed by **Otto Stern**. A schematic representation of this experiment is shown in Figure 1.9. In an oven metal is vaporized by means of high temperature and a collection of the shields with small holes is used to select a narrow beam of atoms. The atoms pass a system of two discs rotating with the same angular

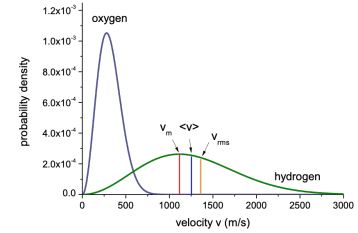


Figure 1.7: Distributions of molecular speeds in atmosphere

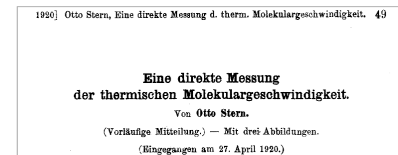


Figure 1.8: Publication by Stern in 1920.

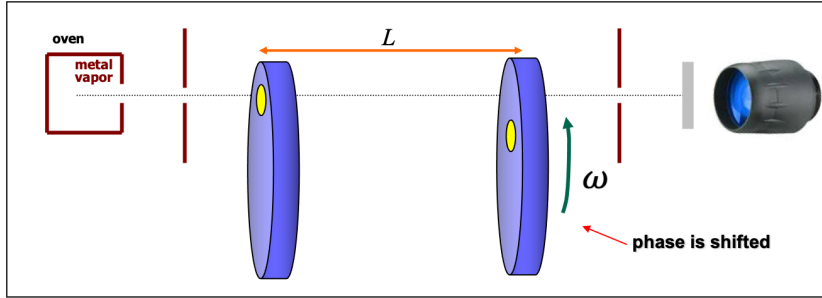


Figure 1.9: Schematics of the Otto Stern's experiment

velocity and each containing a hole. The holes are found at identical distances from the rotation axis but are shifted such that the line connecting them is not parallel to the axis of rotation. The beam passing the first hole may pass the second one if only the rotation speed and the beam speed are finely matched. The intensity of the beam passed both holes can be detected by optical or other means. Thus, by varying the rotation speed the distribution of atomic speeds can be measured.

• **EXERCISE 1.1. 1:**

Prove that the distribution function  $F(v)$  as given by Eq. 1.32 is normalized.

For proving

$$I = \int_0^{\infty} F(v) dv = 1 \quad (1.38)$$

we will need to evaluate the integral

$$\int_0^{\infty} x^2 e^{-bx^2} dx \quad (1.39)$$

Let us use for this purpose the known result

$$\int_0^{\infty} e^{-bx^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{b}} \quad (1.40)$$

and differentiate both sides with respect to  $b$ :

$$-\int_0^{\infty} x^2 e^{-bx^2} dx = -\frac{\sqrt{\pi}}{4} b^{-3/2} \quad (1.41)$$

Hence,

$$I = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{\sqrt{\pi}}{4} \left( \frac{2kT}{m} \right)^{3/2} = 1 \quad (1.42)$$

- **EXERCISE 1.1. 2:**  
Prove Eq. 1.37 by direct calculations.

Differentiating Eq.1.41 with respect to  $b$  yields

$$\int_0^{\infty} x^4 e^{-bx^2} dx = \frac{3\sqrt{\pi}}{8} b^{-5/2} \quad (1.43)$$

Hence,

$$\langle v^2 \rangle = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{\sqrt{3\pi}}{8} \left( \frac{2kT}{m} \right)^{5/2} = \frac{3kT}{m} \quad (1.44)$$

### 1.1.6 Maxwell-Boltzmann distribution

So far we have assumed that, due to chaotic and isotropic motion of particles, the pressure exerted to the container walls was irrespective of position along the wall. In this scenario, the experiment showing that the weight of the reservoir containing some gas (see Figure 1.10) is given by the sum of the weights of the reservoir itself and of all gas molecules appears to be very confusing. The answer is given by the Boltzmann (or more generally by the Maxwell-Boltzmann) distribution of the particle concentration in the presence of a force field. In particular, in the gravity field the particle density decreases with increasing distance for the Earth surface.

- **EXPERIMENT:**

A reservoir with the volume of 2.3 L is vacuumated and placed on a scale. The reading is set to zero. Afterward, the valve is opened to let air in and is closed again. The reading is 2.6 g.

**EVALUATION:**

Explain how the air molecules contained in the reservoir "transfer" their weights to the scale.

Let us use the experimental observation of the Figure 1.10 as a starting point for deriving the Boltzmann distribution (later we re-derive this law in a more rigorous way). The only option that the air molecules contribute to the total weight of the reservoir is to assume that the pressure exerted to the upper and lower parts of the reservoir are different and the latter is higher. Thus, the pressure imbalance times area should be equal to the total gravity force on all air molecules. Let us for the sake of clarity consider a cylindrical reservoir with the basement area  $A$  and height  $h$  and containing  $N$  particles of mass  $m$ . By assuming the occurrence of the pressure gradient along  $y$ -axis collinear with the cylinder axis, we may write:

$$(P(y) - P(y + dy)) A = M(dy)g \quad (1.45)$$

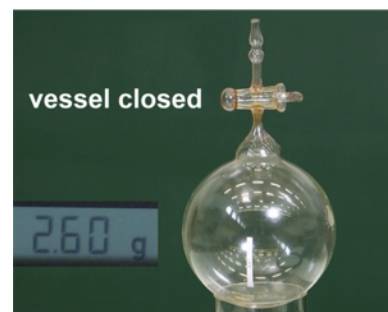


Figure 1.10: Weight of air contained in a 2.3 L reservoir. ©Axel Märcker, UL

By using  $P = nkT$  and  $M(dy) = n(y)mAdy$  Eq. 1.45 can be transformed to

$$\frac{dn(y)}{dy} = -\frac{mg}{kT}dy \quad (1.46)$$

whose solution is

$$\frac{n(y)}{n_0} = \exp\left\{-\frac{mgy}{kT}\right\} \quad (1.47)$$

where  $n_0$  denotes the particle concentration at  $z = 0$ . The equation can be generalized to any force or potential field as

$$n(y) = n_0 \exp\left\{-\frac{U(y)}{kT}\right\} \quad (1.48)$$

In fact, the Boltzmann distribution of the particle concentration in a force field and the Maxwell distribution of particle velocities are intimately related and the former is simply a consequence of the latter under equilibrium conditions. Indeed, the Maxwell distribution of velocities is irrespective of the potential field and is only a function of temperature. If a force field is switched on, then particles are accelerated by this field in certain directions resulting in the particle fluxes. Thus in the gravity field all air molecules would be accelerated toward the Earth surface. Because there is no spatial dependency of the velocity distribution, increasing particle concentration in the flux direction will give rise to increasing flux in the opposite direction. This transient process will stop when the fluxes in the opposite directions become identical. This can be seen as a *detailed balance principle* stating that in equilibrium each elementary process should be equilibrated by its reverse process. In the context of our discussion this principle applies to the particle fluxes.

Let us consider it in some more detail with the help of Figure 1.11. The downward particle flux  $dj_{\downarrow} \equiv dN_{\downarrow}/dt$  of the particles having a velocity components between  $v_i$  and  $v_i + dv_i$  across area  $A$  is

$$dj_{\downarrow} = Av_y dn(v_x, v_y, v_z) = Av_y n_y F(v) dv_x dv_y dv_z \quad (1.49)$$

Here,  $y$ -axis is associated with the vertical perpendicular to  $A$ . The upward flux of the same ensemble of particles is given by the same expression

$$dj_{\uparrow} = Av'_y dn(v_x, v'_y, v_z) = Av'_y n_y F(v) dv_x dv'_y dv_z \quad (1.50)$$

where the prime symbol explicitly indicates that the  $y$ -component of the velocity is positive. According to the detailed balance principle, in equilibrium each such elementary process, e.g. an upward flux, is balanced by a reverse one,  $dj_{\downarrow} = dj_{\uparrow}$ . Let us take account of

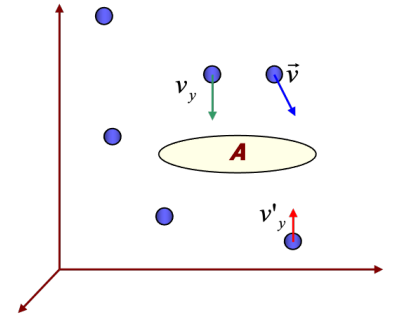


Figure 1.11: Particles crossing area  $A$  in the presence of a force field

the existence of the potential field  $U(y)$  (without loss of generality we assume that  $U$  is constant in the  $xz$ -plane). Because the total energy of the particles is conserved, then

$$\frac{mv^2}{2} + U(y) = \frac{mv'^2}{2} + U(y') \quad (1.51)$$

By evaluating differentials on both sides it is seen that

$$v_y dv_y = v'_y dv'_y \quad (1.52)$$

Thus, the flux equivalency yields

$$n(y)F(v) = n(y')F(v') = n(y')F\left(-\frac{mv'^2}{2kT}\right) \quad (1.53)$$

Let us fix the potential energy at  $y'$  to zero denote the particle concentration at  $y'$  as  $n_0$ . With Eq. 1.51, Eq. 1.53 may now be rewritten as

$$n(y)F\left(-\frac{mv^2}{2kT}\right) = n_0F\left(-\frac{mv^2}{2kT} - \frac{U(y)}{kT}\right) \quad (1.54)$$

which results in Eq. 1.48. Thus, quite generally the Maxwell-Boltzmann law can be expressed as

$$dn = n_0 \exp\left\{-\frac{E_{total}}{kT}\right\} d^3v \quad (1.55)$$

with the Boltzmann and Maxwell distributions being its specific limits.

Interestingly, the Boltzmann distribution of particle concentration in a force field has been used by **Jean Perrin** to determine the Boltzmann constant  $k$  (or the Avogadro number). By measuring the difference in the number of gamboge particles in water at separation of  $30 \mu\text{m}$  due to the gravity field (Figure 1.12) he has obtained  $k = 1.13 \times 10^{-23} \text{ J/K}$  which is a very accurate estimate of the accepted value  $k = 1.38 \times 10^{-23} \text{ J/K}$ .

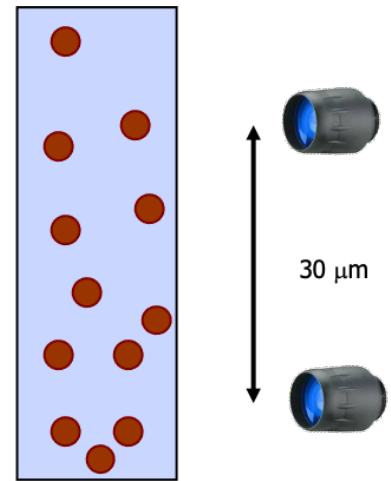


Figure 1.12: Set-up of the Perrin's experiment

### 1.1.7 Collisions

The gas pressure on the walls is determined by both the momentum transfer during elementary collision event and the collision frequency. Let us find the collision frequency  $z$ , which is the number of collision with a unit area per unit time. For training purposes it is instructive to consider first the constant speed case, i.e. when all molecules have identical speeds, but move isotropically. Recalling the derivation of pressure and with Figure 1.13 the number of collisions  $N_i$  during a time interval  $\Delta t$  with the area element  $A$  for particles having  $y$ -component of the velocity  $v_{yi}$  is equal to

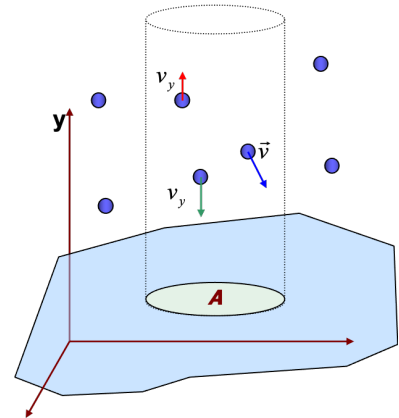


Figure 1.13: Collisions with a wall



$$N_i = n_i A v_{yi} \Delta t \quad (1.56)$$

The collision frequency is found by summing up over all velocities

$$z = \frac{\sum N_i}{A \Delta t} = \sum_i n_i v_{yi} \quad (1.57)$$

or in integral form

$$z = n \int_{-\infty}^0 v_y f(v_y) dv_y \quad (1.58)$$

where  $n$  is the total concentration of particles and  $f(v_y)$  is the relative fraction of particles having  $v_y$  ( $\int_{-\infty}^{\infty} f(v_y) dv_y = 1$ ). The problem is thus to find the distribution of  $v_y$  if  $v$  is fixed. For isotropic systems it is seen from Figure 1.14 that

$$f(v_y) dv_y = \frac{2\pi v_x ds}{4\pi v^2} = \frac{2\pi v \cos(\theta)}{4\pi v^2} v d\theta \quad (1.59)$$

where  $ds$  is the ring thickness on the sphere corresponding with  $dv_y$ . With  $v_y = v \sin(\theta)$

$$z = \int_0^{\pi/2} \frac{v}{2} \sin(\theta) \cos(\theta) d\theta = \frac{1}{4} n v \quad (1.60)$$

The pre-factor 1/4 is not intuitively clear. Indeed one may think that we may divide the entire ensemble of particles onto 6 sub-ensembles moving along the coordinate axis only. In that case only 1/6 part can reach the surface. The exact calculations taking account of the isotropic character of particle movements lead to 1/4. If there will be any distribution of the speeds, then the collision frequency is simply found by taking average over all velocities

$$z = \frac{1}{4} n \langle v \rangle \quad (1.61)$$

The latter can also be proven by direct integration of Eq. 1.58 with the use of Eq. 1.30.

• **EXERCISE 1.1. 3:**

Evaluate the collision frequency by directly using the Maxwell distribution.

$$z = n \sqrt{kT/2\pi m} = n \langle v \rangle / 4$$

• **EXERCISE 1.1. 4:**

The walls of a reservoir containing a rarified gas at concentration  $n_0$  are kept at a temperature  $T$ . In the wall there is a small hole with a radius  $r$  as shown in Figure 1.15. Find the particle escape law from the reservoir. The volume of the reservoir is  $V$ .

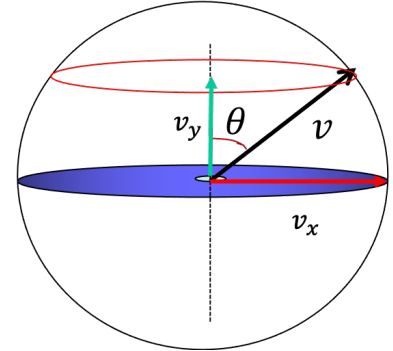


Figure 1.14: Distribution of velocities

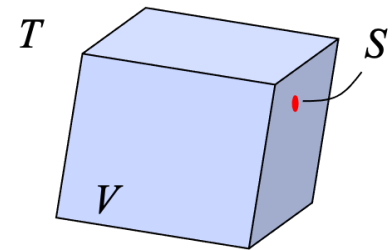


Figure 1.15: Particles escaping through a hole

The number  $dN$  of particles crossing the hole in a time interval  $dt$  is

$$dN(t) = z\pi r^2 dt = \frac{1}{4}n(t)\langle v \rangle \pi r^2 dt \quad (1.62)$$

By dividing both sides by  $V$ , this equation modifies to

$$\frac{dn(t)}{n(t)} = \frac{1}{4V}\langle v \rangle \pi r^2 dt \quad (1.63)$$

whose solution is

$$n(t) = n_0 e^{-t/\tau} \quad (1.64)$$

where  $\tau$  is

$$\tau = \frac{4V}{\langle v \rangle \pi r^2} \quad (1.65)$$

• **EXERCISE 1.1. 5:**

What is the average kinetic energy  $\langle \varepsilon \rangle$  of the particles escaping the reservoir through the hole in the preceding exercise?

One may intuitively think of  $3kT/2$  because in the reservoir each particle has this energy and when they by chance pass the hole they still will have the same energy. One needs however be careful, because the energy of  $3kT/2$  refers to the *average* energy. Keeping in mind the distribution of particle speeds, these are the faster particles in the entire ensemble which have higher chances to find the hole, hence to carry a higher with.

According to Eq. 1.60, the collision frequency  $z(v)$  of the particles having velocity  $v$  with the hole with the cross-sectional area  $A = \pi r^2$  is

$$z(v) = \frac{1}{4}n(v)vA \quad (1.66)$$

where  $n(v)$  is the concentration of particles with  $v$ . To find the average kinetic energy  $\langle \varepsilon \rangle$  of the escaping particles,  $\langle v^2 \rangle$  needs to be evaluated. Note the average needs to be taken over the ensemble of particles crossing the hole:

$$\langle v^2 \rangle = \frac{\int_0^\infty v^2 z(v) F(v) dv}{\int_0^\infty z(v) F(v) dv} \quad (1.67)$$

which is simplified to

$$\langle v^2 \rangle = \frac{\int_0^\infty v^3 F(v) dv}{\int_0^\infty v F(v) dv} \quad (1.68)$$

By dividing the integration result

$$\int_0^\infty v^3 F(v) dv = \frac{4}{\pi^2} \left( \frac{2\pi kT}{m} \right)^{3/2} \quad (1.69)$$

by Eq. 1.36 the average kinetic energy is found to be

$$\langle \varepsilon \rangle = 2kT \quad (1.70)$$



Figure 1.16: An insulating box with a hole shut by a particle gun.

• EXERCISE 1.1. 6:

Initially empty made of an insulating material has a small hole. A gun shuts a particle beam with a concentration  $n_0$  and velocity  $v_0$  as shown in Figure 1.16. Find the temperature established in the box if the mass of each particle is  $m$  and the particle concentration in the box  $n$ .

The particle number conservation requires that

$$n_0 v_0 = \frac{1}{4} n \langle v \rangle \quad (1.71)$$

where  $n$  and  $v$  are the concentration and velocity of the particles escaping the reservoir. After equilibration, the kinetic energy should also be conserved:

$$n_0 v_0 \frac{1}{2} m v_0^2 = \langle E_k \rangle \quad (1.72)$$

where  $E_k$  is total energy flow (per unit time) out of the box. With the result of Eq. 1.70,

$$\langle E_k \rangle = \frac{1}{4} n \langle v \rangle 2kT \quad (1.73)$$

Thus, the energy conservation yields readily

$$T = \frac{m v_0^2}{4k} \quad (1.74)$$

With  $\langle v \rangle = v_0 \sqrt{2/\pi}$

$$n = \sqrt{8\pi} n_0 \quad (1.75)$$

## 1.1.8 Molecular collisions

A smell of coffee or perfume propagates in a room at notably lower speeds as compared to the predictions based on the average molecular velocities. The reason for this is that the molecules do not propagate along straight tracks, but collide with other molecules and change continuously their directions as shown in Figure 1.17. Let us estimate the collision frequency. Let us consider a molecule with a diameter  $d$  moving along a line. It will collide with another molecule of the same diameter if the center of the latter molecule is found anywhere within a circle with the radius  $d$  about the line of movement of the first molecule. Upon collision the molecule of interest changes the flight direction randomly and moves until it collides with the next one. The total length  $L$  covered by the molecule during time  $\Delta t$  is  $L = \Delta t \langle v \rangle$ . The concentration  $n$  of molecules within the tube with volume  $V = L\sigma$ , where  $\sigma = \pi d^2$ , can be found as the number of collisions  $N$  performed by the molecule divided by  $V$ :

$$n = \frac{N}{V} = \frac{N}{\langle v \rangle \Delta t \sigma} \quad (1.76)$$

By noting that  $N/\Delta t$  is nothing else than the collision frequency  $z$  we find its good estimate

$$z = n \langle v \rangle \sigma \quad (1.77)$$

The model we just considered is simplified in a sense that it assumes that the target molecule is moving in a bath of other molecules with the spatially fixed positions. Let us consider the fact that the rest of molecules also move and their speeds are distributed according to the Maxwell distribution. If so, the average speed  $\langle v \rangle$  shall be replaced by the average relative speed  $\langle v_r \rangle$  of the target molecule with respect to the ones of other molecules. For the velocities of two molecules are uncorrelated

$$\langle v_r^2 \rangle = \langle \vec{v}_r^2 \rangle = \langle (\vec{v}_1 - \vec{v}_2)^2 \rangle = 2 \langle v^2 \rangle \quad (1.78)$$

If the system temperature is held constant, then any average velocities should differ only by numerical factors. Thus, the ratio of the average mean square and square of the average velocity is

$$\frac{\langle v^2 \rangle}{\langle v \rangle^2} = \frac{3\pi}{8} \quad (1.79)$$

With Eq. 1.78, the same as well is valid for the relative velocity:

$$\frac{\langle v_r^2 \rangle}{\langle v_r \rangle^2} = \frac{3\pi}{8} \quad (1.80)$$

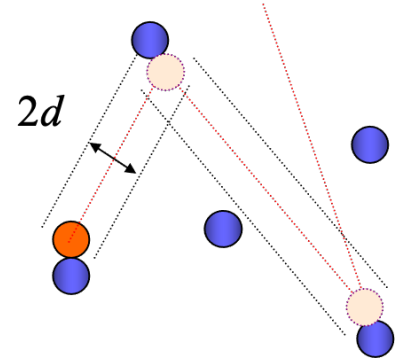


Figure 1.17: Particle collisions

Finally, this yields  $\langle v_r \rangle = \sqrt{2}\langle v \rangle$  and

$$z = \sqrt{2}n\langle v \rangle\sigma \quad (1.81)$$

### 1.1.9 Mean free path length

A very important concept in the molecular collisions theory is the mean free path length  $\lambda$  (m.f.p.l.), which is the average distance the molecules travel between two subsequent collisions. It can easily be found by dividing the

$$\lambda = \frac{\langle v \rangle t}{\sqrt{2}n\langle v \rangle\sigma t} = \frac{1}{\sqrt{2}n\sigma} \quad (1.82)$$

Let us with the help of Eq. 1.83 and  $P = nkT$  estimate typical m.f.p.l. in, e.g., nitrogen gas at normal conditions:

$$\lambda \approx \frac{1.4 \times 10^{-23} \cdot 300}{1.4 \cdot 10^5 \cdot 3.14 \cdot 13 \times 10^{-20}} \approx 70\text{nm} \quad (1.83)$$

where the diameter of nitrogen molecule 365 pm was used. As we see, with this extremely short  $\lambda$  the molecular pathways become frequently broken and the trajectory appears to be very chaotic. Exactly due to this fact, to displace by 1 m a nitrogen molecule at ambient conditions will need more than one hour, which is by far exceeds  $t = L/\langle v \rangle \approx \text{ms}$  if the were no molecular collisions. Derivation of the respective laws will be covered in the subsequent chapter.

### 1.1.10 The light mill

Before analyzing how the m.f.p.l. determines such processes as mass transfer, viscosity or heat conduction, let us explore some phenomena which rely on relatively long m.f.p.l. or relevant at relatively low pressure. Let us consider first the so called Crookes' radiometer or light mill shown in Figure 1.18. It is made of a frictionless propeller with the wings silvered on the one side and covered black on the other side and placed in a reservoir with a rarified gas. After exposing the mill to a light source it starts to rotate. A few experimental observations help to sort out the origin of the mill rotation:

- The rotation frequency is higher for with infrared radiation rather than with ultraviolet. This means that this is not caused by any kind of light pressure for the UV-photons are more energetic.
- The direction of rotation towards the mirrored part helps also rationalizing that the phenomenon is not caused by a higher momentum transfer upon molecular collisions at the mirrored side as compared to the black side.

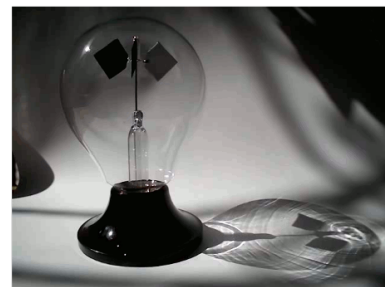


Figure 1.18: The light mill

- The rotational speed increases with decreasing pressure, i.e. the phenomenon is not related to higher temperature of the gas near the black side. Another argument against this scenario is that in the presence of temperature gradient concentration of the gas molecules change respectively to vanish the pressure gradient.
- If instead of the light source to use a cold reservoir with liquid nitrogen, the mill starts rotating in opposite direction, suggesting that the will rotation is not due to evaporation of some molecules adsorbed in carbon black.

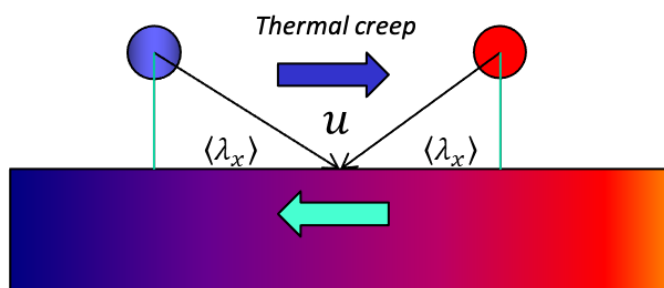


Figure 1.19: Thermal creep

In fact rotation of the mill is caused by *thermal creep*. Remarkably, the unbalanced forces due to thermal creep appear only at the edges of the wings and not on the wings' faces! Let us consider the origin of this phenomenon based on the drawing of Figure 1.19. It shows a substrate with a temperature gradient across it. The gas molecules at the hotter end have on average higher kinetic energy than at the colder side, hence also higher average velocity. Let us consider some point or small spot on the substrate. The molecules arriving from the hotter regions and colliding with it supply higher tangential momentum to the substrate than those approaching from the colder part. Hence, the substrate experiences a net force caused by the molecular collisions pointing toward the colder side. But the substrate is fixed and cannot move. Therefore, the colliding molecules will experience an opposite force from the substrate giving rise to a net flux of the molecules toward the hotter part. This is called thermal creep. When the process attains its stationary character with the average creep speed  $u$ , the momentum transfer to the substrate should vanish. This condition can be quantified by considering the aforementioned spot located at  $x$  and two planes separated by a distance  $\langle \lambda_x \rangle$  to the left (colder side) and to the right (hotter side). The molecules coming to the spot on the substrate from that planes will not experience collisions with other molecules anymore. No momentum transfer can thus be expressed as

$$\langle v_x \rangle (x - \langle \lambda_x \rangle) + u = \langle v_x \rangle (x + \langle \lambda_x \rangle) - u \quad (1.84)$$

By noting that  $\langle \lambda_x \rangle$  are typically notably smaller than the system sizes, this equation can be rearranged to

$$\frac{\langle v_x \rangle (x + \langle \lambda_x \rangle) - \langle v_x \rangle (x - \langle \lambda_x \rangle)}{2\langle \lambda_x \rangle} = \frac{d\langle v_x \rangle}{dx} = \frac{u}{\langle \lambda_x \rangle} \quad (1.85)$$

Thus, the creep velocity, which is indicative of the rotations of the mill, is

$$u = \langle \lambda_x \rangle \frac{d\langle v_x \rangle}{dx} \quad (1.86)$$

By differentiating Eq. 1.79 and by using  $\langle v \rangle^2 \approx 3\langle v_x \rangle^2$ , the derivative in the preceding equation can be replaced by

$$\frac{d\langle v_x \rangle}{dx} = \frac{d\langle v_x \rangle}{dT} \frac{dT}{dx} = \frac{\sqrt{3}\pi}{16} \frac{1}{\langle v \rangle} \frac{d\langle v^2 \rangle}{dT} \frac{dT}{dx} \quad (1.87)$$

With  $\langle \lambda_x \rangle \approx \sqrt{3}\lambda$

$$\frac{d\langle v^2 \rangle}{dT} = \frac{3k}{m} \quad (1.88)$$

the creep speed results as

$$u = \frac{9\pi}{16} \frac{kT}{P} \sqrt{\frac{\pi k}{8m}} \frac{dT}{dx} \propto \frac{T^{1/2}}{P} \frac{dT}{dx} \quad (1.89)$$

Thus, the effect turns out to be inversely proportional with pressure in accord with the experimental observations and stronger with increasing temperature and temperature gradient. The latter is easy to rationalize because with the higher gradients the imbalance in the forces applied to the surface, hence to the molecules too, becomes stronger. The  $P^{-1}$ -law is less intuitive. If the pressure is relatively high, i.e. the m.f.p.l. is short, then the intermolecular collisions will cause efficient temperature equilibration in the gas above the substrate. Hence, the effect is only observed at relatively low gas densities. Remarkably, the thermal creep occurs along the wings' edges only (not facets!) and this appears to be enough to see a macroscopic effect.

~

• EXERCISE 1.1. 7:

Find relationship between  $\langle v \rangle^2$  and  $\langle v_x \rangle^2$ .

When the m.f.p.l. becomes comparable to the mill size the effect is proportional to  $P$ .

## 1.1.11 Other effects in rarified gases

In rarified gases infrequent collisions prohibit the formation of macroscopic fluxes, this may give rise to interesting phenomena. Let us consider two reservoir kept at different temperatures as shown in Figure 1.20 and connected by a tube with a diameter  $d \gg \lambda$ . A higher pressure established in the reservoir 2 will give rise to a transient macroscopic flux through the tube (by pushing the molecules in analogy with the piston considered earlier) until the pressure equilibrates. In this case, the pressure constancy is fulfilled when

$$n_1 T_1 = n_2 T_2 \quad (1.90)$$

If the hole is small such that  $d < \lambda$  no pressure gradient across the tube can be created. Thus, thermodynamic equilibrium will be established when the fluxes through the tube in opposite direction become identical. If both reservoirs contain the same gas, the equilibrium condition is given by

$$n_1 \sqrt{T_1} = n_2 \sqrt{T_2} \quad (1.91)$$

which is different from Eq. 1.90! If initially both reservoirs contained the same amounts of gas, i.e. the particle concentration were identical, after they are connected there will be a particle flux from the hotter reservoir to the colder one. However, if the gases pressures were initially identical, then a flux from the colder to the hotter reservoir is created. In a similar manner one may consider a scenario when the reservoirs contain different gases, leading to the equilibrium condition of

$$n_1 \sqrt{\frac{T_1}{m_1}} = n_2 \sqrt{\frac{T_2}{m_2}} \quad (1.92)$$

In this case, if initially the reservoirs contained different gases at identical pressures and temperatures, there will be a higher flux of molecules with the smaller mass through the tube.

- EXPERIMENT:

Figure 1.21 demonstrates a glass cylinder filled with a helium gas at room temperature and atmospheric pressure situated about a ceramic cylinder containing very small pores. The cylinder is hollow and contains normal air. The higher flux of He molecules across the ceramic cylinder walls increases the pressure inside which is seen by water displaced out of the lower container.

- EVALUATION:

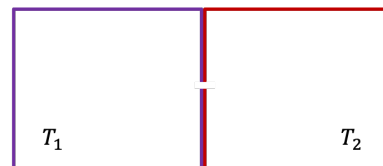


Figure 1.20: Two reservoirs with different temperatures connected by a tube.

The vacuum flasks exploit the low gas density to suppress convection as the most efficient mechanism of heat exchange.



Figure 1.21: Pressure created due to flux imbalance of He and air through a porous membrane. ©Axel Märcker, UL



## 1.2 Diffusion

Diffusion, or mass transfer due to chaotic motion of molecules, is most omnipresent phenomenon in nature. The concept is, of course, much broader than as applied to tiny atoms, molecules or bigger particles. It has found many applications for describing the processes on financial markets, distribution of diseases, migration of nations and languages and so on. In the context of the kinetic gas theory, diffusion plays a very special role for it led to the acceptance of the existence of atoms. Specifically, this is the random walk approach to diffusion. Ultimately, the solution of this problem provided by Einstein in 1905, is considered as the very first, indirect visualization of molecular trajectories, hence the existence of molecules.

### 1.2.1 Fick's laws of diffusion

Let us first consider a classical treatment of diffusion, the process often related to equilibration of a concentration gradient. For the sake of simplicity we confine ourselves to one-dimensional case, for higher dimension the results are similar. Fig. 1.22 shows schematically two regions with the higher and lower concentrations of particles. You may think of as on the left side you have a higher concentration of ink (pigment particle or dye molecules) in water. Assume now that, because of thermal energy, the particles move chaotically. Chaotically means that there is no preference for moving to the right over moving to the left. Hence, just because the concentration difference, there will be a net diffusion flux  $J$  of the particles to the right. The first Fick's law postulates that this flux is directly proportional to the concentration gradient:

$$J = -D \frac{\partial c}{\partial x} \quad (1.93)$$

In Eq. 1.93  $D$ , the coefficient of proportionality, is the diffusion coefficient or simply diffusivity. The first Fick's law postulate thus that the flux is a linear response to the concentration gradient. The minus sign indicates that the flux is towards the regions with lower concentrations.

Eq. 1.93 can be combined with the law of the matter conservation to yield an equation describing the concentration evolution in time. Let us consider a slice of length  $\Delta x$  and of unit height (in one-dimensional case this equivalent to an interval  $\Delta x$ ). The total number of particles  $n$  in this slice is  $c\Delta x$ . Because of the concentration gradient, number of particles entering the slice from left and from right are different. Hence, during a time interval  $dt$ , the total amount of particles in the slice changes by  $dn = dc\Delta x = (J(x) - J(x + \Delta x)) dt$ .

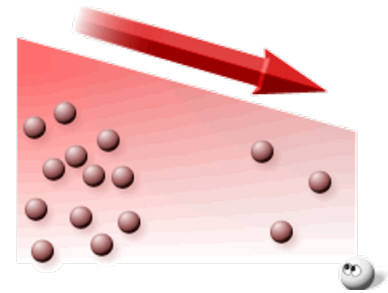


Figure 1.22: Concentration gradient

By concentration  $c$  the number of particles per unit volume is referred to. By flux  $J$  we refer to the number of particles crossing unit area per unit time.

Hence, the matter conservation law can be expressed as

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \quad (1.94)$$

By substituting Eq. 1.93 into Eq. 1.94 one obtains the Fick's second law of diffusion or diffusion equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1.95)$$

Note that for deriving Eq. 1.95 we have assumed that  $D$  is constant and is not a function of position  $x$  and, hence, concentration. This differential equation describes how initially created concentration profile  $c(x, t = 0)$  will evolve in time. As the most important example, for  $c(x, t = 0) = \delta(x)$  the solution of the diffusion equation for any spatial dimension  $d_s$  is

$$c(x, t) = (4\pi Dt)^{-d_s/2} \exp\left\{-\frac{r^2(t)}{4Dt}\right\} \quad (1.96)$$

This equation, in particular, describes a spread (concentration profile) of an initially small spot of ink in water. An important quantity characterizing this Gaussian function is the distribution width

$$\langle r^2(t) \rangle = 2d_s Dt \quad (1.97)$$

On considering the way how Eq. 1.95 was derived, one may get an impression that, for having the process of diffusion, one always needs a macroscopic gradient in concentration or concentration inhomogeneities. This is not explicitly true. Diffusion, or more precisely, self-diffusion occurs also under equilibrium conditions. The governing equation in this case is the same, Eq. 1.96, but instead of  $c(x, t)$  another quantity, namely probability density  $\rho(x, t)$  to find a particle at  $x$  at time instant  $t$  which at  $t = 0$  was found at  $x = 0$ , is used.

Let us consider a process in which particles may perform steps of a length  $l$  every time unit in any direction and the step lengths distribution function is  $\zeta(l)$  (probability that in a random move the step length is  $l$ ). Because we are dealing with the probabilities,  $\int_{-\infty}^{\infty} \zeta(x) dx = 1$ . Let us require the process being unbiased, i.e.  $\int_{-\infty}^{\infty} x \zeta(x) dx = 0$ . In addition, we ask the integral  $\int_{-\infty}^{\infty} x^2 \zeta(x) dx = a^2$  being finite. There are physical processes, such that  $\zeta(x)$  have long algebraic tail so that the latter integral diverges. They are out of the scopes of this chapter. Let us find an equation describing evolution of the probability density function  $\rho(x, t)$  to find the particle at the position  $x$  at the time instant  $t$ .

For the derivation, let us evaluate  $\rho(x, t + \Delta t)$ , given that  $\rho(x', t)$  is known. By referring to Figure 1.23, it can be represented as an integral

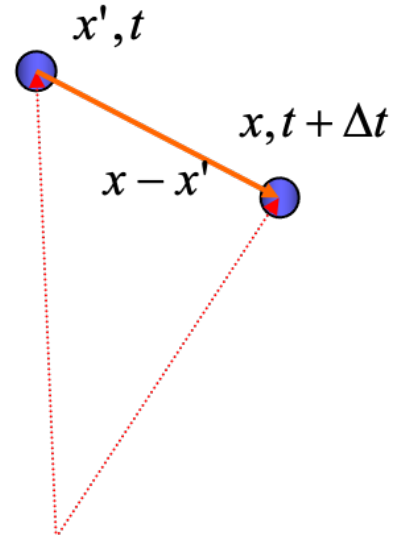


Figure 1.23: Particle displacement

$$\rho(x, t + \Delta t) = \int_{-\infty}^{\infty} \rho(x', t) \zeta(x - x') dx \quad (1.98)$$

This equation tells that you may find the particle at  $x$  whenever an appropriate movement brings it to  $x$  from any initial position  $x'$ . The "appropriate movement" is given by the probability  $\zeta(x - x')$  to have the exactly needed step length  $x - x'$ . The integral may be further evaluated by introducing a new variable, displacement  $z$ , which is  $z = x - x'$ . With  $z$ , Eq. 1.98 becomes an integral over displacements

$$\rho(x, t + \Delta t) = \int_{-\infty}^{\infty} \rho(x - z, t) \zeta(z) dz \quad (1.99)$$

The function  $\rho(x - z, t)$  can be expanded in a series around  $x$  and only first non-vanishing terms considered:

$$\rho(x, t + \Delta t) = \int_{-\infty}^{\infty} \left( \rho(x, t) - \frac{\partial \rho(x, t)}{\partial x} z + \frac{1}{2} \frac{\partial^2 \rho(x, t)}{\partial x^2} z^2 \right) \zeta(z) dz \quad (1.100)$$

The first term on the right hand side of Eq. 1.100 is  $\rho(x, t)$ , the second term is zero and the third term is  $\frac{a^2}{2} \frac{\partial^2 \rho(x, t)}{\partial x^2}$ . Eq. 1.100 can be rearranged and written as

$$\frac{\rho(x, t + \Delta t) - \rho(x, t)}{\Delta t} = \frac{a^2}{2\Delta t} \frac{\partial^2 \rho(x, t)}{\partial x^2} \quad (1.101)$$

Finally, by introducing the coefficient of self-diffusion  $D = a^2/2\Delta t$  one obtains the equation

$$\frac{\partial \rho(x, t)}{\partial t} = D \frac{\partial^2 \rho(x, t)}{\partial x^2} \quad (1.102)$$

which is found to coincide with the diffusion equation, Eq. 1.95.

- **EXPERIMENT:**

One may drop a small amount of ink onto water surface. The evolution of the color profile is governed by the diffusion equation.

**EVALUATION:**

Try to see that the ink front propagates following a  $t^{1/2}$ -law.

Strictly, the integration in Eq. 1.99 needs to be performed from  $\infty$  to  $-\infty$ . Because we deal with the unbiased processes, so that all even moments are non-zero and odd moments are zero, the integration can equally be shown in a more convenient form.

### 1.2.2 Trajectory analysis

Just by looking at the macroscopic diffusion equation one hardly may conclude about the existence of atoms or molecules. The missing connection was provided by Einstein, who has shown that a statistical analysis of the random trajectories of molecules, if they really were

present, would lead to the same equations discussed in the preceding section.

Let us consider the problem of random walks along a line as an instructive model. Each unit of time we will move randomly to the left or to the right. The step length is fixed to  $l$  and the initial position to zero. Note, choosing the initial position at  $x = 0$  means that any subsequent position  $x$  at any time  $t$  is as well the displacement. The movement direction can easily be determined by coin flips, delivering a random variable  $s = 1$  or  $s = -1$  depending on the face the coin ends with on a table. Let us first consider a single trajectory, which is a position  $x$  of the particle after  $N$  steps. Obviously,  $x(N) = l \sum_{n=1}^N s_n$  and is a quantity fluctuation about zero. If we perform ensemble average, i.e. repeat the experiment many times and evaluate  $\langle x(N) \rangle$  we end with a trivial, almost non-informative zero value. The only useful information surviving is that the process is unbiased, i.e. the probabilities stepping to the left and to the right are identical and equal to  $1/2$ .

- **EXPERIMENT:**

An example of a random, Brownian trajectory one may see on the video showing chaotic motion of a milk droplet.

**EVALUATION:**

- **EXAMPLE 1.2.1:**

Evaluate  $\langle x(N) \rangle$ .

**SOLUTION:**

$\langle x(N) \rangle = l \langle \sum_{n=1}^N s_n \rangle$ . One may now split the sum onto two terms, where the first sum will run only over events corresponding with  $s = 1$  and the second one with  $s = -1$ . Then it is easy to see that the two terms are equal to the total number of trials  $N^+$  delivered  $s = 1$  and  $N^-$  delivered  $s = -1$ . Thus,  $\langle x(N) \rangle = l (\langle N^+ \rangle - \langle N^- \rangle)$ . For an unbiased process  $\langle N^+ \rangle = \langle N^- \rangle$ , hence  $\langle x(N) \rangle = 0$ .

Hence, one needs to evaluate another quantity which is not averaged out to zero. One of the possible candidates is the module  $\langle |x| \rangle$ , which, however, is too tedious to evaluate mathematically. Another option is the mean square displacement (MSD)  $\langle x^2(N) \rangle = l^2 \langle s^2(N) \rangle$ . The solution of this problem can easily be obtained by deriving a recurrence series. Let us start first evaluating MSD after one step, e.g. for  $N = 1$ . Let us do  $K$  experiments in total to evaluate the ensemble average. Out of  $K$  experiments, there will be  $K^+$  results with  $s = 1$  and  $K^-$  results with  $s = -1$ . The average is evaluated as

Very interesting and reach physics emerges if the step length and/or jump times are distributed.



Figure 1.24: Random number generator

$$\langle s^2(N=1) \rangle = \frac{K^+(+1)^2 + K^-(-1)^2}{K} \quad (1.103)$$

The ratios  $p^+ = K^+/K$  and  $p^- = K^-/K$  for large  $K$  may be considered as the respective probabilities that in a single trial one finds  $s = 1$  or  $s = -1$ . In our case  $p^+ = p^- = 1/2$ , therefore

$$\langle s^2(N=1) \rangle = p^+ + p^- = 1 \quad (1.104)$$

To obtain  $\langle x^2(N=2) \rangle$  one needs to consider two consecutive trials, thus

$$\langle s^2(N=2) \rangle = p^+p^+(+2)^2 + p^+p^-(0)^2 + p^-p^+(0)^2 + p^-p^-(-2)^2 = 2 \quad (1.105)$$

Similarly

$$\langle s^2(N=3) \rangle = 2 \left( (p^+)^3(+3)^2 + 2(p^+)^2p^- (+1)^2 + p^+(p^-)^2(-1)^2 \right) = 3 \quad (1.106)$$

It is thus evident that  $\langle s^2(N) \rangle = N$ .

Finally,  $N$  can be replaced by  $t/\tau$ , where  $\tau$  is a time interval to perform one single movement, so that

$$\langle x^2(t) \rangle = \frac{l^2}{\tau} t \equiv 2Dt \quad (1.107)$$

where we have defined the coefficient  $D = l^2/(2\tau)$ . Note that this quantity coincides with Eq. 1.97! Thus, statistical analysis of random trajectories leads to the same physical picture described by the Fick's diffusion law.

### 1.3 1st law of thermodynamics

Thermodynamics is a subject dealing with transfer of heat from one body to another. If the older theories of thermodynamics, sometime quite successful, were based on an invisible substance called caloric, the analysis done in the preceding sections unequivocally related heat to kinetic energy. We have seen that the kinetic theory of gases yielded microscopic understanding of many processes. The analysis was, however, quite tedious for already relatively simple phenomena. Henceforth, we now will be seeking for a more "easy" frameworks to analyze different processes related with heat transfer. From time to time we will, however, refer to the kinetic theory to establish microscopic mechanisms underlying some processes.

#### 1.3.1 Heat

In order to increase temperature of a body by  $\Delta T$  some amount of heat needs to be supplied. The heat is typically measured in Joules [J] or calories [cal]. The latter is equal to 4.184 J, the amount needed to increase temperature of 1 g of water by 1 K. Our everyday experience tells us that different materials may need for that different amounts of heat  $Q$  per unit mass. Indeed, the coefficient of proportionality  $c$  between  $Q$  and  $m\Delta T$ ,

$$Q = mc\Delta T \quad (1.108)$$

which is known as *specific heat* varies from material to material. As we will see it in more detail later, one needs distinguish between specific heats for the heat transfer processes performed at constant pressure ( $c_p$ ) and constant volume ( $c_V$ ). Thus,  $c_p$  for hydrogen gas and for gold differ by two orders of magnitude being 14.3 J/gK and 0.13 J/gK, respectively. The same is noticed by comparing materials being in the same thermodynamic state, like wood and aluminum with  $c_p$  equal to about 2 J/gK and 0.9 J/gK, respectively.

For measuring specific heats, the calorimetric devices are typically used. In this setup, one uses a substance with known heat capacity enclosed in an insulated box to elucidate the heat capacity of another material by letting them equilibrate their temperatures. Typically, water is used as the reference substance for its specific heat is nearly temperature-independent. Let us assume that water initially had a higher temperature of  $T_{wi}$  than that of the material under study  $T_{mi}$ . Placing the latter into water results in the temperature equilibration, which finally becomes  $T_f$ . The amount of heat consumed by the material obviously must equal that released by water. The heat balance equation is then rather simple:

In calorimeters the reservoir itself may also release or consume heat. This value per unit grad is carefully measured and supplied with the calorimeter's technical details.

$$m_w c_{pw} (T_{wi} - T_f) = mc_p (T_f - T_{mi}) \quad (1.109)$$

It is worth noting that Eq. 1.108 holds only if the material under study does not change its phase state upon changing temperature. Perhaps the simplest experiment demonstrating this is measuring water temperature on heating. First the temperature rises until boiling point and afterward temperature remains constant and equal to  $100^\circ\text{C}$ . As this temperature is approached all supplied heat is used to evaporate water. The same if to heat ice - at  $0^\circ\text{C}$  its temperature does not change and ice melts. The heat used for phase change is called *latent heat*.

### 1.3.2 Heat conduction

If wood may store more energy per unit mass than aluminum, why do we sense aluminum to be colder upon touching it with our fingers? The answer is that we probe not the amount of heat stored but how quickly the material absorbs heat. For metals the heat transfer turns out to be very efficient. To define thermal current  $I \equiv \dot{Q}$  ( $[\text{J}/\text{s}=\text{W}]$ ) consider a drawing of Figure 1.25. In a way similar to the mass transfer (recall we have mentioned that mass and heat transfer have much in common), the total flux of heat across cylinder can be expressed in analogy to the first Fick's law (linear response) as

$$I = -kA \frac{dT}{dx} \quad (1.110)$$

where  $k$  is thermal conductivity [ $\text{W}/\text{mK}$ ].

Consider two geometrically identical cylinders (length  $l$  and cross-sectional area  $A$ ) made of aluminum and copper are connected serially and the two sides are kept at temperatures of  $100^\circ\text{C}$  and  $0^\circ\text{C}$  as shown in Figure 1.26. Find the temperature  $T_i$  at the interface between two metals. A constant heat flow  $I$  will be established across the composite material. For the two parts, Eq. 1.110 is

$$\begin{cases} -T_i + 100^\circ\text{C} = \frac{l}{k_{al}A} I \\ T_i - 0^\circ = \frac{l}{k_{co}A} I \end{cases} \quad (1.111)$$

By solving the systems of two equations the temperature at the interface is found to be  $34.7^\circ$ . In the problem just considered one may refer to the coefficient  $l/(kA)$  as to thermal resistivity  $R$ . Interestingly then, the effective resistivity of the combined cylinder  $R_{eff}$  is given by the sum of the individual resistivities of the two cylinders. This can be generalized for serial connection of resistivities as

$$R_{eff,serial} = \sum_i R_i \quad (1.112)$$

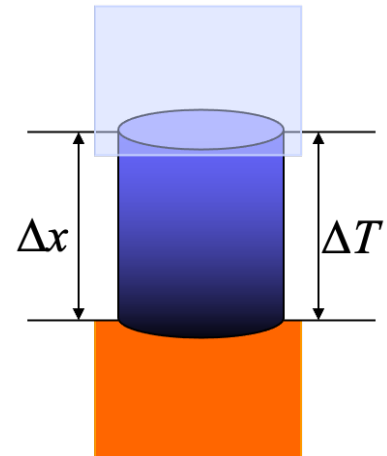


Figure 1.25: Heat flow across cylinder

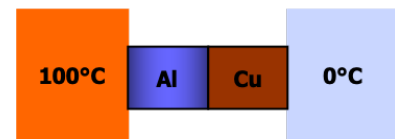


Figure 1.26: Contact between two metals

If the cylinders are connected in parallel, the temperature gradient is constant and one obtains

$$R_{eff,parallel} = \sum_i R_i^{-1} \quad (1.113)$$

- **EXERCISE 1.3. 1:**  
Derive Eqs. 1.112 and 1.112.

### 1.3.3 The first law of thermodynamics

The first law of thermodynamics is nothing else than the law of conservation of total energy formulated on a "thermodynamic language". It says that all heat  $Q$  supplied to a system equates the change of the internal energy  $\Delta U$  of the system plus work  $W$  done by the system,

$$Q = \Delta U + W \quad (1.114)$$

Note that the work done by the system can be both positive (*the system does work*) or negative (*work done on the system*). Eq. 1.114 rewritten for infinitesimally small changes is

$$\delta Q = dU + \delta W \quad (1.115)$$

From a purely mathematical perspective, the symbol  $\delta$  used to denote small increments instead of typically used  $d$  indicates that the functions  $Q$  and  $W$  are not differentiable. From the thermodynamic viewpoint this means that they are not *state functions* in contrast to  $U$ . While the latter is fully determined by the current set of thermodynamic parameters, such as  $P$ ,  $V$  and  $T$ , the formers are not and depend on how this state was approached. Treating  $Q$  as differentiable function may lead to severe misinterpretations.

In the first part of the course, we will consider only ideal gases following the Boyle's law. For ideal gases the internal energy is contributed solely by the kinetic energy of the molecules. Henceforth,  $U$  of an ideal gas placed in an insulated reservoir cannot depend on the volume of the reservoir. It was indeed proven in experiments done already back to mid of 19th century, where it was observed that upon expanding the gases most closely fulfilling the ideal gas law did not change their temperature.

The work done by gas to expands the system by  $dV$  if pressure is  $P$  is found conventionally as  $PdV$ .

Interestingly, as we will see later, simple division of  $\delta Q$  by  $T$  makes it state function.



### 1.3.4 Heat capacities

By definition, the heat capacity is amount of heat needed to increase temperature of the system:

$$c = \frac{\delta Q}{dT} = \frac{dU}{dT} + P \frac{dV}{dT} \quad (1.116)$$

Let us find first a general equation valid for any gases, including the real ones. For this, let us assume that  $U = U(V, T)$  is a function of both volume and temperature. Then,

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (1.117)$$

Dividing both sides by  $dT$  yields

$$c = \left( \frac{\partial U}{\partial T} \right)_V + \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \frac{dV}{dT} \quad (1.118)$$

It turns that the heat capacity at constant volume,  $c_v$ , is simply related to the variation of the internal energy with temperature,

$$c_v = \left( \frac{\partial U}{\partial T} \right)_V \quad (1.119)$$

On considering the heat capacity at constant pressure, it is given by

$$c_p = c_v + \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_p \quad (1.120)$$

Let us evaluate it for ideal gas. Because for ideal gas  $U$  is a function of temperature only, the partial derivative in the square brackets is zero. On the other hand, for one mole of gas

$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{P} \quad (1.121)$$

Hence, for ideal gas

$$c_p = c_v + R \quad (1.122)$$

which is known as the Mayer's equation.

### 1.3.5 Work done by ideal gas

Work  $W$  done by gases during any arbitrary processes are obtained as an integral

$$W = \int P(V, T) dV \quad (1.123)$$

Schematically it represents the area under the function  $P(V)$  on the PV-diagram as exemplified in Figure 1.27 for the combined isobaric-isochoric and isochoric-isobaric processes and for isothermal process. Because in all these processes the initial and final states do coincide, but the areas not, this proves that the work is not *state function*. Indeed, it depends on the way how two states are connected, which is, however, irrespective of the connecting path for the state functions.

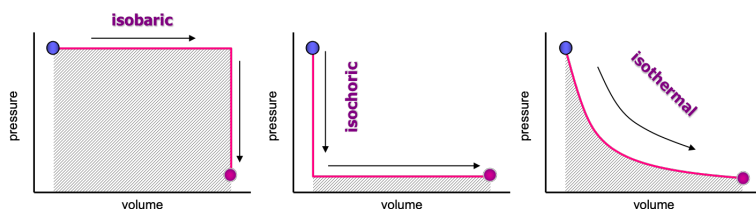


Figure 1.27: Work done during selected processes

Because no work is done during isochoric processes and for isobaric processes work is simply pressure times the pressure difference, it turns out that gas performs higher work along isobaric expansion at high pressure followed by isochoric pressurization ( $W = P_1(V_2 - V_1)$ ) rather than by first pressurizing it and then expanding ( $W = P_2(V_2 - V_1)$ ). Isothermal expansion yields an intermediate result ( $W = RT \ln(v_2/V_1)$ ).

### 1.3.6 Adiabatic processes

Among important quasistatic, reversible processes adiabatic ones, in which during the process no heat is supplied to or removed from the system, play an important role. In this case, Eq. 1.115 becomes

$$c_v dT + PdV = 0 \quad (1.124)$$

For a mole of ideal gas

$$dT = \frac{pdV + VdP}{c_p - c_v} \quad (1.125)$$

By combining Eqs. 1.124 and 1.125 and by introducing the adiabatic constant  $\gamma \equiv c_p/c_v$ , an equation describing adiabatic processes in ideal gas is found as

$$\gamma PdV + VdP = 0 \quad (1.126)$$

Thus, during adiabatic processes the following quantities  $PV^\gamma$ ,  $TV^{\gamma-1}$ , and  $P^{\gamma-1}T^{-\gamma}$  remain unchanged. Because the internal energy of ideal one-atomic gases is simply equal to their kinetic energy

( $3RT/2$  for one mole of gas),  $c_v = 3R/2$ . With the Mayer's equation it follows then than for one-atomic gases  $\gamma = 5/3$ . For diatomic gases the rotational degrees of freedom add to  $c_v = 5/2$ , hence  $\gamma = 7/5$ .

## 1.4 2nd law of thermodynamics

On its own, the 1st law of thermodynamics is unable to predict the direction of the processes. It states only that the total amount of energy remains constant, but cannot predict whether heat will flow from cold to hot body or from hot to cold body. To add direction is the goal of 2nd law.

### 1.4.1 Different formulation of the 2nd law of thermodynamics

Let us consider a quasi-static, cyclic process schematically represented in Figure 1.28 in a  $PV$ -diagram. In the first part, the path '1a2', some amount of heat  $Q_1$  is supplied to the system. This energy obtained in the form of heat equals the work  $W_1$  done by the system plus change of the internal energy from  $U_1$  to  $U_2$ . Let us now return the system back to its original state. In doing so, however, we aim purposefully at extracting some useful net work resulting from the entire cycle. Thus, the work  $W_2$  done on the system to return it in its original state should be smaller than  $W_1$ . To achieve this, the system may be brought into contact with a cold reservoir to cool the system down, i.e. to extract some amount of heat  $Q_2$ . This will correspond with the path '2b1' such, that the area under this curve is lower than that under '1a2'. The net work  $W = W_1 - W_2$  extracted is given then by the area enclosed by the loop '1a2b1'. The energy balance for one cycle is

$$\oint \delta Q = \oint dU + \oint \delta W \quad (1.127)$$

Because internal energy  $U$  is the state function, its loop integral is zero. Hence, for the example just considered Eq. 1.127 becomes

$$Q_1 - Q_2 = W_1 - W_2 \quad (1.128)$$

Let us consider the efficiency  $\eta$  of this cycle. It is instructive in this regard to consider cars working on a fuel. The source of  $Q_1$  is the energy released during burning of the fuel. The cooler, where  $Q_2$  goes to, is the surrounding atmosphere. This example suggests that it is reasonable to define the efficiency as the useful work per unit  $Q_1$ , i.e. which fraction of  $Q_1$  obtained can be converted to useful work:

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - |Q_2|}{Q_1} \quad (1.129)$$

It is very attractive to have a device which entirely converts heat to net work, i.e. having  $\eta = 1$ . Unfortunately, this is prohibited by the 2nd law of thermodynamics postulating that *no cyclic process with  $\eta = 1$  is possible*. There are many other formulations of this

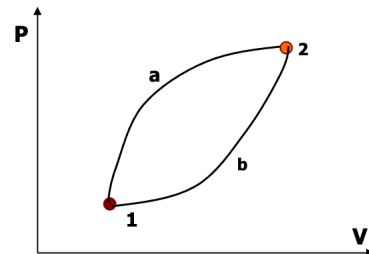
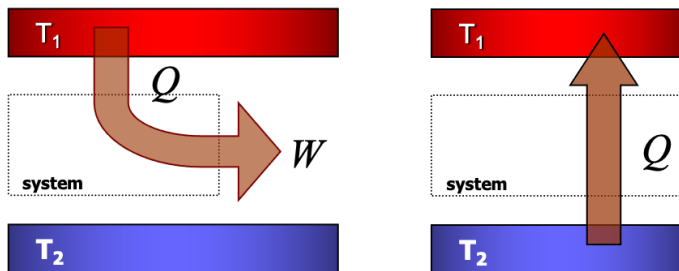


Figure 1.28: An arbitrary cyclic process

postulate, but all they turn out to be equivalent. Among them it is worth mentioning three historically important formulations by

- *Lord Kelvin*: No cyclic process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work (see Figure 1.29)
- *Planck*: It is impossible to construct a device, which is operating in a cycle, the sole result of which will be lifting up a weight due to a decrease of an internal energy of the heat bath
- *Clausius*: No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature (see Figure 1.29)



The Kelvin's formulation coincides with our statement that  $\eta < 1$

Figure 1.29: Kelvin's (left) and Clausius's (right) statements of the 2nd law

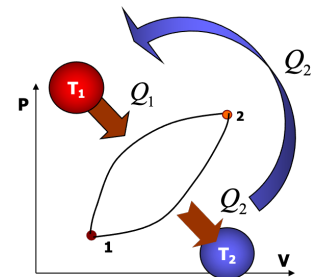


Figure 1.30: Equivalency of the Kelvin's and Clausius's statements

It's easy to see that all these formulations are equivalent. Let us consider, for example, schematics in Figure 1.30 and assume that the Clausius's device is possible. Let us consider another device taking  $Q_1$  from hot reservoir, doing some work  $W$  and giving  $Q_2$  to cold reservoir. Let us now connect the Clausius device to the first one and pump amount of heat  $Q_2$  from the cold to hot reservoir. In the whole cycle, thus,  $Q_1$  is entirely converted to  $W$ , which violates the Kelvin's postulate. This proves that both statements are equivalent. The same can be shown for any other pairs.

#### 1.4.2 The Carnot cycle

Among a variety of the cyclic processes, the Carnot cycle shown in Figure 1.31 plays a very distinguished role. It represents a cycle with the highest possible efficiency, henceforth often called an *ideal cycle*. Also, its efficiency does not depend on the particular details of the system. Indeed, as we show in what follows its efficiency is sole function of the hot and cold reservoir temperatures.

Let us analyze it in more detail by using ideal gas as a working substance. The cycle is composed of four branches:

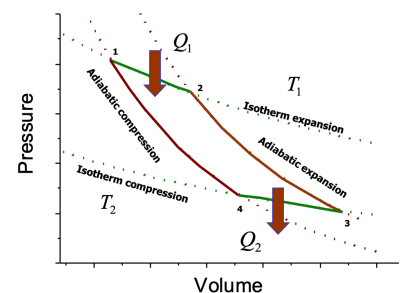


Figure 1.31: The Carnot cycle

1. *Isothermal expansion*: During this process temperature is held constant and the heat  $Q_1$  supplied to the systems goes to work  $W_1$  done by the gas while the internal energy remains unchanged.

$$Q_1 = W_1 = \int_{V_1}^{V_2} PdV = \nu RT_1 \ln(V_2/V_1) \quad (1.130)$$

where  $\nu$  is the number of moles.

2. *Adiabatic expansion*: In this part, the internal energy of the gas is used to do work, i.e. to expand the system further. No heat exchange with outer world is allowed. The process is thus described by  $TV^{\gamma-1} = \text{const.}$

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad (1.131)$$

3. *Isothermal compression*: The amount of heat  $Q_2$  is removed from the system, work  $W_2$  is done on the system.

$$|Q_2| = |W_2| = \int_{V_3}^{V_4} PdV = \nu RT_2 \ln(V_3/V_4) \quad (1.132)$$

4. *Adiabatic compression*: In this last step, the system is returned to its original state by compressing the gas adiabatically.

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1} \quad (1.133)$$

Finally, the efficiency is obtained as

$$\eta = \frac{Q_1 - |Q_2|}{Q_1} = 1 - \frac{T_2 \ln(V_3/V_4)}{T_1 \ln(V_2/V_1)} \quad (1.134)$$

By dividing Eq. 1.131 by Eq. 1.133 it is seen that  $V_2/V_1 = V_3/V_4$ , hence

$$\eta_{Carnot} = 1 - \frac{T_2}{T_1} \quad (1.135)$$

Indeed, the efficiency is found to be sole function of the two bath temperatures, but not the system parameters like pressure or volume. Note also, even though for the sake of simplicity we have consider an ideal gas, the final result will not change. Indeed, the variation of the internal energy over entire cycle is zero. Hence, the assumption made in the derivations above that internal energy does not depend on the system volume is not critical.

Before considering how the Carnot cycle could be used to formulate one of the central consequences of 2nd law, let us pay attention to another aspects. Because the efficiency of the Carnot cycle is irrespective of the substance, it can be applied to assess some general properties. Let us consider a particular example and derive a general equation relating some measurable properties of materials to the

difference  $c_p - c_v$  of the specific heat capacities at constant pressure and volume. A general expression for it has been obtained earlier, see Eq. 1.120. In that expression, the partial derivative

$$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V_0 \quad (1.136)$$

i.e. it is related to the thermal expansion coefficient  $\alpha$ , which is a measurable quantity and is tabulated for many materials. What remains unknown in Eq. 1.120 is the partial derivative  $(\partial U/\partial V)_T$ .

Let us consider a substance working on a Carnot cycle. The cycle can be subdivided onto many smaller ones all being Carnot cycles by adding families of isotherms and adiabatic functions (see Figure 1.32~). If the area enclosed by a sub-cycle is relatively small, then the area, i.e. work  $W$ , can be approximated as

$$W \approx (P_1 - P_x)(V_2 - V_1) \quad (1.137)$$

Note that  $\Delta P = P_1 - P_x$  represents the pressure difference at constant volume. Because the pressures  $P_1$  and  $P_x$  corresponds with the isotherms having  $T_1$  and  $T_2$ , respectively,  $\Delta P$  can be found as

$$\Delta P = \left(\frac{\partial P}{\partial T}\right)_V (T_2 - T_1) \quad (1.138)$$

Thus, the net work  $W$  done in the sub-cycle is

$$W = \left(\frac{\partial P}{\partial T}\right)_V (T_2 - T_1) (V_2 - V_1) \quad (1.139)$$

The amount of heat  $Q_1$  supplied to this sub-system equals the change of internal energy and work done by the sub-system,

$$Q_1 = \Delta U + P_1(V_2 - V_1) \quad (1.140)$$

Because this done along an isotherm,

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_T (V_2 - V_1) \quad (1.141)$$

For the Carnot cycle

$$\frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} \quad (1.142)$$

By substituting all functions found earlier into this equation one finds the identity

$$T_1 \left(\frac{\partial P}{\partial T}\right)_V = P_1 + \left(\frac{\partial U}{\partial V}\right)_T \quad (1.143)$$

Because the initial point of the sub-cycle can be selected arbitrarily, the indices at  $P_1$  and  $T_1$  can be dropped out. Notably, the right hand

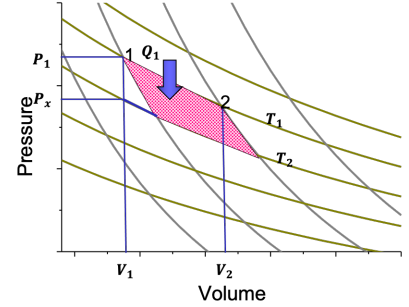


Figure 1.32: Collection of Carnot cycles

side of this equation is exactly the missing part in Eq. 1.120. Thus, we obtain finally

$$c_p - c_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \quad (1.144)$$

With the use of the chain rule it can alternatively be represented as

$$c_p - c_v = -T \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P^2 \quad (1.145)$$

In particular, in Eq. 1.145  $c_p - c_v$  is related to the isothermal compressibility and thermal expansion coefficients.

The chain rule says

$$\left( \frac{\partial z}{\partial x} \right)_y \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x = -1$$

- **EXERCISE 1.4. 1:**  
Prove the chain rule.



## 1.5 Entropy

We have finally approached a point where we will establish how the 2nd law of thermodynamics dictates directions of thermodynamics processes by introducing the concept of entropy. The central in this route will be the Clausius inequality.

### 1.5.1 The Clausius inequality

Let us consider a cyclic process composed of two devices - the first working in the direct cycle and producing work  $W_1$  and the second one in the reverse cycle, i.e. using the work  $W_1$  produced by the first device to pump heat from the cooler to the heater as shown in Figure 1.33. The energy balance for the entire cycle is

$$W_2 - W_1 = Q_1 - |Q_2| - |Q'_1| + Q'_2 \quad (1.146)$$

Let us consider the reverse cycle to be the Carnot cycle. For the latter

$$\frac{Q'_2}{|Q'_1|} = \frac{T_2}{T_1} \quad (1.147)$$

By combining Eqs. 1.146 and 1.147, the amount of heat  $Q'_1$  is related to the parameters of the direct cycle as

$$|Q'_1| = \frac{T_1}{T_1 - T_2} (Q_1 - |Q_2|) \quad (1.148)$$

Let us now find the amount of heat  $Q_1 - |Q'_1|$  taken from the heater in one entire cycle:

$$Q_1 - |Q'_1| = \frac{T_1 T_2}{T_1 - T_2} \left( \frac{|Q_2|}{T_2} - \frac{Q_1}{T_1} \right) \quad (1.149)$$

The left hand side of Eq. 1.149 is less or equal to zero. Notably, zero results if the direct cycle is also working along a Carnot process (in that case the term in brackets on the right hand side is zero). As well,  $Q_1 - |Q'_1|$  cannot be positive. Otherwise it would immediately violate the 2nd law of thermodynamics in the Clausius's formulation. Indeed, in that case with zero net work done heat is pumped from cold to hot reservoir. Thus, keeping also in mind that  $T_1 > T_2$ , quite generally for any arbitrary process

$$\frac{|Q_2|}{T_2} - \frac{Q_1}{T_1} \leq 0 \quad (1.150)$$

This inequality is referred to as the *Clausius inequality*. One particular consequence of Eq. 1.150 is that it states that the efficiency of any arbitrary process cannot exceed that of the ideal Carnot cycle.

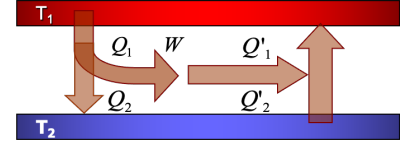


Figure 1.33: A combined cycle

Eq. 1.150 can easily be generalized to any cyclic processes (e.g. composed of many different sub-cycles):

$$\oint \frac{\delta Q}{T} \leq 0 \quad (1.151)$$

### 1.5.2 Entropy

Let us consider one cycle of a quasistatic, reversible process (see Figure 1.34). If to integrate  $\delta Q/T$  along all states encountered, one finds

$$I_d = \oint \frac{\delta Q}{T} \quad (1.152)$$

If the reverse process is performed, the integral is

$$I_r = \oint \frac{-\delta Q}{T} \quad (1.153)$$

This only possible if  $I_d = I_r = 0$ . By exploiting this idea, it is easy to prove then that the integrals along any reversible processes connecting two states a and b in Figure 1.35 yield identical results. The independency of the integral on the pathway means that the ratio  $\delta Q/T$  is a full differential. It is denoted by  $dS$ , where the new variable (or function)  $S$  is called *entropy*. Because it is uniquely defined for any state and is irrespective of how this state was approached, entropy is the state function. Note, like potential energy, it is defined to accuracy of a constant.

Just by using the definition of entropy, it is easy to calculate it if  $P(V, T)$  is known. Let us do it as example for ideal gas. The basic equation to start with is

$$TdS = c_v dT + PdV \quad (1.154)$$

For any arbitrary process

$$\Delta S = c_v \int_{T_1}^{T_2} \frac{dT}{T} + \int_{V_1}^{V_2} \frac{RT}{V} dV = c_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right) \quad (1.155)$$

In particular, for the first and the second terms on the right hand side of Eq. 1.155 would describe isochoric and isothermal processes respectively. For isobaric processes (see Figure 1.36),

$$dS = \frac{\delta Q}{T} = c_p \frac{dT}{T} \quad (1.156)$$

The integration yields

$$\Delta S = c_p \ln \left( \frac{T_2}{T_1} \right) \quad (1.157)$$

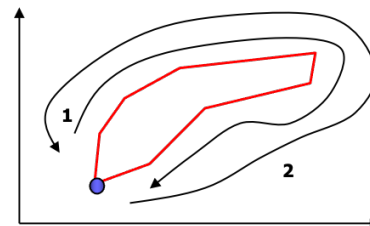


Figure 1.34: A quasistatic, reversible cycle

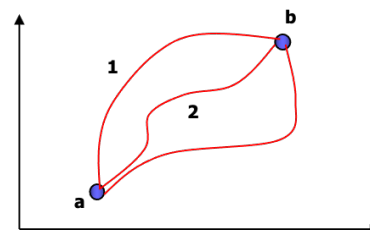


Figure 1.35: Different reversible processes connecting two states

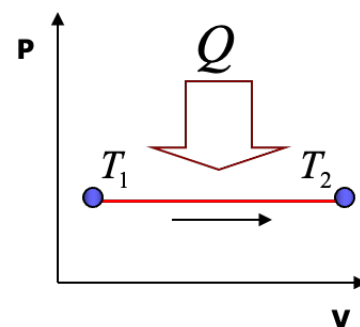


Figure 1.36: Isobaric heating

During any reversible adiabatic process entropy of the system does not change while no heat added to or removed from the system. Hence, these processes occur at constant entropy and the process may also be referred to as an *isentropic* process.

### 1.5.3 Reversible vs. irreversible processes

Let us consider a classical problem of two connected reservoirs with gas initially filling only one of them as shown in Figure 1.37. Reasonably, the gas will expand and distribute homogeneously over two reservoirs. A justified question is whether this process can be reversible, i.e. would it be possible that the gas may recollect to fill only one of the reservoirs? It turns out that entropy decides whether a process in a *closed system* can take place or not. Let us consider for this the diagram in Figure 1.38. It shows two states, initial 'a' and final 'b', connected by a reversible, isothermal process indicated by the red line. During this process, some amount of heat  $Q$  is supplied and entropy of the system increases by  $S_b - S_a = Q/T$ . Let us ask ourselves whether any process occurring without heat exchange with the external bath, i.e. adiabatic one (not necessarily reversible!), may return the system to its original state 'a'? The answer is given by the Clausius inequality stating that

$$\int_b^a \frac{\delta Q}{T} + \int_a^b ds \leq 0 \quad (1.158)$$

Because the process is adiabatic, the first term on the left hand side of the inequality is zero. Hence, if the process is allowed, then  $\int_a^b ds \leq 0$  and  $S_b \leq S_a$ ! Thus, such a spontaneous process would be possible if during that process entropy of the closed system would decrease. For the particular case indicated in Figure 1.38 by the purple line, resulting in entropy decrease, the process is disallowed by the Clausius inequality. The same is obviously valid for recollecting gas in one side only - in such process entropy would decrease.

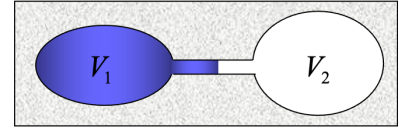


Figure 1.37: Two reservoirs with gas filling only one of them

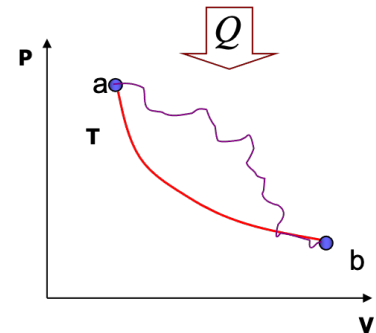


Figure 1.38: Two state connected by reversible and irreversible processes



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